Potentiometric Performances of Thiuram Sulphides as Coated-wire Ion Selective Electrode for Ag (I) ions

A

Thesis Submitted

in partial fulfillments of requirements for the

Degree of

Master of Science in Chemistry

Submitted By
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Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled **"Potentiometric Performances of Thiuram Sulphides as Coated-wire Ion Selective Electrode for Ag(I) Ions"**, in partial fulfillment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry (SCB), Thapar University, Patiala, is my own work during the period of Jan 2009 to May 2009, under the supervision of Dr. Ashok Kumar S.K., Lecturer, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this dissertation for the award of any other degree.

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Date: 18 - 6 - 2009

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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This is to certify that the project entitled **"Potentiometric Performances of Thiuram Sulphides as Coated-wire Ion Selective Electrode for Ag(I) Ions"**, being submitted by Ms. Manjusha in partial fulfillment of the requirement for the award of degree of Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonifide work carried out under the supervision of Dr. Ashok Kumar S.K. and that no part of this project has been submitted for the award of any other degree.

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Thesis Abstract

A new wire coated silver ion-selective electrode with a wider concentration range(10^{-6} M-10^{-1} M) was developed using TMTMS & TETDS as a neutral carrier. An optimum mixture of PVC, neutral carrier, plasticizer (NPOE) was used in preparing the coating. The effect various parameters, such as the coating composition and solution pH on the efficiency of the electrode are described. It has shown slope of 60mv/decade over a concentration range 10^{-1} M-10^{-6} M with TETDS and slope of 59mv/decade over a concentration range 10^{-1} M-10^{-5} M with TMTMS. The selectivity co-efficient of the electrode towards various interfering ions, response time were estimated. The developed electrode used as an excellent indicator electrode.

Chapter –1

Introduction

1.1 Electroanalytical Techniques

Metals play an important role in many life processes. Even some essential metal ions exhibit toxicity above the elevated levels. Unlike other pollutants metals non-biodegradable, may undergo transformations and can have large environmental and economic impact. Environmental analysis has become an area of interest for scientists. These demands have led to the development of many important analytical approaches. The realization of importance of analytical methods in present day life has lead to vigorous efforts by chemists and instrumentalists to develop new instruments, techniques and procedures so as to make analysis convenient, fast, reliable and selective. Various instrumental techniques such as Atomic Absorption Spectrophotometry (AAS), Inductively Coupled Plasma-atomic Emission Spectrophotometry (ICP-AES), Fluorimetry, Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), Electron Spin Resonance Spectroscopy (ESR), Cyclic Voltammetry (CV) and many more are available for analytical chemists. Although these methods provide sensitive and reproducible results, requirement of expensive infrastructure led to the development of Chemical Sensors. Sensors constitute one of the simpler approaches to chemical analysis: they permit direct assay of a gas or liquid sample, without prior sample preparation or purification. For the applied scientist, their special attraction is due to the ease with which they can perform assays away from a central laboratory and with minimum requirement for reagents or complex apparatus. In recent years, strenuous efforts have been made towards the fabrication of cheap, disposable, operationally simple sensor systems for such field use.

1.2 Potentiometric Sensors

Electrochemical sensors are the largest and oldest group of chemical sensors (1-3). Many members of this have reached commercial maturity while many are still in various stages of development. They are developed by their mode of measurements into potentiometric (measurement of voltage), amperometric (measurement of current) and conductometric (measurement of conductivity) sensors. Potentiometry is of great practical importance, is a zero current technique in which the information about the sample composition is obtained from the measurement of potential established across a membrane material, possessing different ion recognition processes and have been developed to impart high selectivity. Electrochemical processes take place at the electrode solution interface. The distinction between various electrodes and analytical techniques reflects the type of electrical signal used for the quantification. The two principal types of electroanalytical measurements are potentiometric and potentiostatic measurements. Both type of measurements require at least two electrodes (Conductance) and a contacting sample (Electrolyte solution), which constitutes the electrochemical cells. The electrode surface is thus a junction between an ionic conductor and an electronic conductor. One of the two electrodes responds to the target analyte (s) and is thus termed the reference electrode, is of constant potential (i.e., independent of the properties of the solution). The resulting potentiometric probes have thus been widely used for several decades for direct monitoring of ionic species like cations viz., alkali, alkaline earth and transition metal ions and anions viz., F^-, Cl^-, Br^-, I^-, CN^- etc.

1.3 Ion Selective Electrodes

Ion-selective membrane is the key component of all potentiometric ion sensors. Ion-selective electrodes (ISEs) are the chemical sensors of longest history and probably the most frequent routine applications. The most attractive features of this technique are the speed with which samples can be analyzed, portability of the device, sample non-destruction, cost effectiveness and also large measuring range. Moreover, their fabrication in the laboratory is quite easy and may become commercially available soon after their development. Therefore, ion selective sensor's utility and simplicity has replaced other wet analytical methods that were often far slower and more cumbersome to perform. Ion-selective electrodes are increasingly used in the fields of environmental, industrial, agricultural and medicinal analysis, process monitoring as well as detectors in HPLC and capillary electrophoresis (CE). Some of the established applications of ISEs are such as determination of F^- in drinking water, Ca^{2+} in dairy products and K^+ in fruit juices. The field of ion-selective membrane research is a vigorous and ever-expanding one. ISEs have been not only practical solutions to a great variety of analytical problems but also useful tools for probing host-guest chemistry. However, research aimed to expand ISEs applications is still flourishing, with the aim of improving their performance, reaching better understanding of their response mechanism and finding new chemical or physical configurations.

1.3.1 Classification of Ion-selective Electrodes (ISEs)

ISEs can be classified into two categories: **Primary ISEs** and **Sensitized ISEs.**

Primary Ion-Selective Electrodes: Primary electrodes have further been divided into two classes:

(a) Solid state Electrodes / Crystalline Electrodes: In these electrodes the physical state of the membrane is usually in solid state. Depending on the composition of the membrane, these are further subdivided into the following two categories:

a. *Homogeneous membrane electrodes:* These are ion-selective electrodes, in which the membrane is a crystalline material prepared from either a single compound or a homogeneous mixture of compounds (e.g., Ag_2S, AgI/Ag_2S).

b. *Heterogeneous membrane electrodes:* The heterogeneous solid-state membranes are fragile and tend to crack on often uses. To adjust this limitation for these inert binders are added. These are ion-selective electrodes prepared of an active substance, or mixture of active substances, mixed with an inert matrix (such as silicone rubber or PVC), or placed on hydrophobized graphite or conducting epoxy resin, to form a heterogeneous sensing membrane. If the amount of the inert matrix is small, the contact between the particles of the electroactive material is maintained throughout the body of membrane.

This inert matrix should be inert, hydrophobic, tough, flexible, and crack resistant and not swell in sample solution.

(b) Liquid Membrane electrodes/Non-crystalline electrodes: The membrane of these electrodes consists of an organic liquid immiscible with water in which an electroactive material, capable of exchange with ions for which the electrode is selective, has been dissolved. Usually the electroactive materials are ion-pairs with the cation or anion having a long hydrocarbon chain. Here the solvent should be chosen in such a way that it should be insoluble in water and is of low viscosity, low vapour pressure and considerable association of the ions in the membranes.

Sensitized Ion-Selective Electrodes (ISEs)

These electrodes are modified form of primary ISEs, for the determination of concentrations of gases and organic molecules rather than of ions. There are two main types of these sensitized ISEs.

(a) Gas sensing electrodes: These are the sensors composed of an ion-selective electrode (indicator electrode) and a reference electrode in contact with a thin film of solution, which is separated from the bulk of the sample solution by a gas-permeable membrane or an air gap.

(b) Enzyme substrate electrode*:* This is a sensors in which an ion-selective electrode is covered with a coating containing an enzyme which reacts with an organic substance (substrate) resulting in a species to which the ion-selective electrode responds. Alternatively, the sensor could be covered with a layer of substrate, which reacts with the enzyme, co-factor, or inhibitor to be assayed.

1.3.2 Response Mechanism of Ion-Selective Electrodes

The electrochemical measuring cell (Figure1) consists of two galvanic half-cells, ion-selective and reference electrodes. A reference electrode is used to measure the working electrode potential of an electrochemical cell. It should have a stable electrochemical potential as long as no current flows through it. The IUPAC representation of cell is:

Ag | AgCl | KCl 3M || bridge electrolyte | sample || membrane || inner filling solution | AgCl | Ag

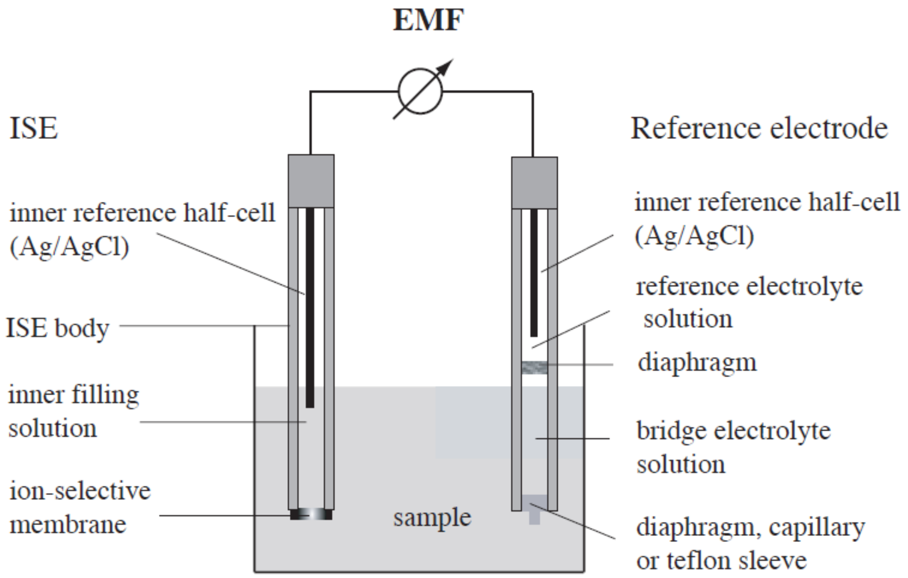


Figure1: Schematic diagram of an ISE measuring cell

The total potential difference (electromotive force, EMF) rising between ISE and reference electrode depends on sample composition and can be measured by voltmeter or by respective multi-channel measuring station. The EMF measured under zero-current conditions between two electrodes is a sum of local potential differences arising at each electrochemical interface:

$$EMF = E_{const} + E_M + E_{D,ref} \text{ ------------ } (1)$$

The only sample dependent potentials are the membrane potential, E_M, and the liquid-junction, or diffusion, potential of the reference electrode, $E_{D,ref}$. All other potentials can be kept constant and represented by E_{const}.

Liquid junction potential originates from the different mobility of ionic species in the sample solution and in the bridge electrolyte of the reference electrode. It can be kept constant by employing concentrated bridge electrolytes with similar mobilities of cations and anions (e.g.1 M KCl, 1M NH_4NO_3 or 1M KNO_3).

1.3.3 Coated-wire Electrodes

Coated-wire electrodes (CWEs) were first introduced in the mid of 1970's by Freiser (4). In the classical CWE design, a conductor is directly coated with an appropriate ion-selective polymer membrane (PVC) to form an electrode system that is sensitive to electrolyte concentrations. The CWE response is similar to that of classical ISE, with regard to detecting ability and range of concentration. The great advantage is that it eliminates the need for an internal reference electrode, resulting in benefits during the desire to miniaturise and mass fabricate sensors has led to the development of potentiometric solid-state sensors with new sensing systems, namely solid contact electrodes (SCEs) (5) such as solid crystal membranes and coated wire electrodes (CWEs). The substrate in the wire type electrodes is usually platinum wire, but silver, copper and graphite rods have also been used. CWEs are manufactured by dipping a metal wire into a solution of the membrane mixture. This is particularly useful for the *in vitro* and *in vivo* biomedical and clinical monitoring of different kinds of analytes.

1.4 Ionophore

Ionophore, or ion carrier, or ligand is the key components of polymeric membrane ion-selective electrodes that govern the ion selectivity and sensitivity because the molecular-level phenomenon sensed by the ISE is the binding between the ionophore and target ion. Ideally, it forms reversible and relatively strong complex with target ion and not with the other ions. There are two kinds of ionophore, charged and neutral carrier. Various substances viz. inorganic and organic ion exchanger, chelating ionophores, solid electrolyte, salts of multivalent atoms, schiff bases, metal chelates, polyaza, polythia macrocycles, crown ethers, cryptands and calixarenes have been used as ion carriers for the preparation of ISEs. To be used as suitable ion carrier; the active sensor material should be physically compatible with the matrix, have a low solubility product, must exhibit some electrical conductivity, have balance between the free energies of ion-ligand interaction, ion-hydration and undergo rapid ion exchange at the membrane sample interface. In order to keep the membrane composition constant, the ionophore must retain within the membrane; therefore, aside from the binding center it must contain numerous lipophilic groups. From a more mechanistic perspective, the potentiometric response of membrane-based ISEs containing a specific ionophore can be used to provide information about the mode of analyte binding as well as, at least potentially, molecular insights into the details of the relevant substrate receptor interactions (6).

The neutral ionophores based on their structural features have been further classified into different categories viz:

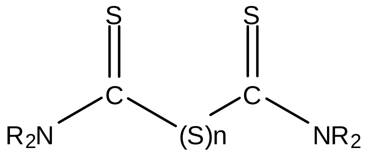
Podands :The acyclic and multiligating and multiarmed molecules.
Coronands :Monocyclic molecules with O, N, S, etc. and their combinations as ligating sites.
Lariats :Coronands with one or more appendages which can participate in binding with the guest.
Cryptands :Bicyclic and polycyclic heteromacrocycles with three-dimensional cavities.
Spherands :The monocyclic receptors with spherical cavities.

Neutral ionophores (also called ionophores), which carry no net charge until complexed with a cation, have led to ISEs with a vide range of selectivities. Three fundamental requirements are mandatory in order to realize such potentiometric sensors:-

1) The ionophore has to be highly lipophilic.
2) The free energy of ligand exchange must be relatively low.
3) The ionophore needs to induce ion-permeability selectivites in sensor membranes. This depends critically on the structure and free concentration of the ionophore in the membrane phase and the partitioning capacity of the solvent mediator.
4) The presence of lipophilic anions incorporated to reduce the interference by lipophilic sample anions and so dislodge interferents from the memberane phase.

1.5 Research Problem

The dithiocarbamates which belong to the organic sulphur compounds possess strong metal binding properties and a capacity to form chelates with many metals as a non-selective complexing agents. On the other hand, the use of thiuram sulphides which contain two moieties of dithiocarbamates would have an enhanced selectivity to metal ions due to the appropriate positions of their two dithiocarbamate groups. Further, the dithiocarbamate derivatives are less soluble in organic solvents, while these thiuram sulphides are soluble in organic solvents. Thiuram sulphides make a useful alternative to the dithiocarbamate derivatives, where it can be used to sense soft metal from the aqueous phase. In this class we have selected two ionophores to prepare coated-wire ion selective electrode for silver ions.



(I) Tetramethylthiuram monosulphide (TMTMS) n=1, $NR_2 = N(CH_3)$

(II) Tetraethylthiuram disulphide (TETDS) n=2, $NR_2 = N(CH_3)_2$

Chapter –2

Literature Survey

Electrodes are devices with which one can detect the movement and separation of charges occurring at phase boundaries, as well as induce and vary such processes by means of a forced current flow the electrode can be a piece of some sufficiently inert conductors such as (Pt, Ag, Cu, etc.) If such an electrode is immersed in an electrolyte solution which contains ions of the electrode material, a potential difference will be develop between electrode and solution which depends on the activity of this particular metal ion in solution. This is referred to as an electrode of the first kind. An inert electrode, such as platinum (in a solution not containing platinum ions) which indicates the oxidizing or reducing power of a specific redox system is called a redox electrode.

If a metal electrode is coated with a thin layer of one of its slightly soluble anion salts (eg. Ag/AgCl), then the potential difference depends on the activity this anion in solution. This is an electrode of the second kind. If the slightly soluble metal salt layer contains yet another cation, which also forms a sparingly soluble salt-with the anion, but has a larger solubility product than the electricity metal-anion salt (for example $Ag/Ag_2S/Cu_2S$), then the potential difference depends on the activity of this cation in solution such a device is an electrode of the third kind. Between the electron-conducting material and the electrolyte there can be many other materials, such as semiconductors, complete insulators like glass and organic compounds. At these phase boundaries a potential difference develops which depends on the activity of a specific ion which is present both in the electrode and in solution, and which can migrate easily between the two phases. Such electrodes which selectively sense a specific ion in the presence of others are called ion selective electrodes.

Coated-wire electrodes (CWEs), introduced by Freiser in the mid 1970s, are prepared by coating an appropriate polymeric film directly onto a conductor. The ion response membrane is commonly based on poly (vinyl chloride), while the conductor can be metallic (Pt, Ag, Cu) or graphite-based of any convectional shape, such as wire or disk. The conductor is usually dipped in a solution of PVC and the active substance, and the resulting film is allowed to air dry. CWEs are extremely simple, inexpensive, and easy to prepare and function were over the 10^{-7}-10^{-1} M concentration range. Coated wire electrodes may suffer from reproducibility and long –term stability problems, resulting from the poorly defined contact and mechanism of charge transfer between the membrane coating and the conducting transducer. Nevertheless, such devices have been found useful for various important applications, provided that the electrodes are calibrated periodically. New concepts for preparing CWEs appear to improve their analytical performance, particularly with respect to stability and reproducibility through the achievement of thermo dynamically defined interferences such ability offers great promise for eliminating study state ion fluxes and hence to lower the detection limits compared to traditional ISE.

The various coated-wire ion selective electrode for Ag^+ ion and other ions (cationsand anions) are described in following tables in the terms operating characteristics (slope, response time, detection limit and selectivity).

Table1: List of coated-wire ion selective electrode using ionophores for Ag^+ ions

Sr. No.	Name of Ionophore	Detection limit (M)	Slope (mV/dec.)	pH range	Selectivity
1	[bis 5-(4-nitrophenyl azo)salisylaldimine] 1,8-diamino, 3,6-dioxo octan (7)	7.8×10^{-7}	56.2	2.5-7	Ag^+ ion
2	2-[(2- 2-[(2-Carboxyphenyl)sulfanyl]ethoxy, ethyl)sulfanyl]benzoic acid (8)	1.2×10^{-8}	59.0	2.5-8.7	Ag^+ ions
3	methyl-2-pyridyl ketone oxime (MPKO) (9)	$1x10^{-6}$	59.8-60.5	2.5-8.5	Ag^+ ions
4	octahydroxycalix[4]arene (10)	2.1×10^{-6}	58.0	1.5-6.5	Ag^+ ions
5	2-mercaptobenzimidazole (MBI) (11)	6.3×10^{-7}	60.0	2-7	Ag^+ ions
6	thiacalix[4]arenas (12)	1×10^{-7}	60.0		Ag^+ ions
7	5,11,17,23-tetra-tert-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28 bis(diphenylphosphinoylmethoxy)calix[4]arene (13)	6.3×10^{-7}	58.4	4-6.7	Ag^+ ions
8	2,8,14,20-tetrabutyl-4,6,10,12,16,18,22,24-octaacetyl-resorc[4]arene (14)	3×10^{-6}	58	1.5-6.0	Ag^+ ions
9	cyclam (1,4,8,11-tetraazacyclotetradecane) (15)	$5 x 10^{-8}$	59	2-8	Ag^+ ions
10	25,27-dihydroxy- 26,28-bis[5-(4-methyl-6-hydroxypurimidine)thiaamyloxy] calix[4]arene (16)	1×10^{-8}	61.4	3.0-7.0	Ag^+ ions

Table2: Ionophore based CWEs for some alkali and alkaline earth metal ions

Sr. No.	Name of ionophore	Detection limit (M)	Slope mV/decade	pH range	Selectivity
1	2,3-Diphenylquinoxaline-4′,4″-dioxytriethylene glycol (17)	6.7×10^{-7}	30	4.1-8.9	Sr(II) ions
2	p-tert-butylcalix[4]arene ethyl ester (18)	1.45×10^{-6}	58.65	3-10	Na^{+} ion
3	N,N′-bis(5-methyl salicylidene)-p-diphenylene methane diamine (19)	2×10^{-6}	29.4	1.7-6	Pb^{2+} ions
4	Benzo-9-crown-3 (20)	1×10^{-6}	29	2-6	Be^{2+} ions
5	Bis(diisobuty1dithiocarbamate (21)	3.2×10^{-6}	28	3.5-5.5	Pb^{2+} ions
6	Bis(crown ether) (22)	1×10^{-4}	57	4-1	Na^{+} ions
7	Hexachloroantlmonate(V) and 1,2,4,6-tetraphenylpyrldlnlum (23)	1×10^{-7}	50		Sb(V)
8	Valinomycin (24)	1×10^{-5}	57	2-10	K^{+} ions
9	5,11,17,23,29,35-Hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene (25)	6×10^{-7}	30	1.5-6	Pb^{2+} ions

Table3: Ionophore based CWEs for some transition metal ions

Sr. No.	Name of Ionophore	Detection limit M	Slope mV/decade	pH range	Selectivity
1	Calix[4]arene (26)	1×10^{-6}	58	1-4	Hg^{2+} ions
2	Poly(4-vinyl pyridine) (27)	0.5×10^{-7}	30	3-4	Hg^{2+} ions
3	5-Amino-3-methylisothiazole (28)	3.9×10^{-7}	29.5	3.3-9	Co^{2+} ions
4	Dibenzo[e,k]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene (29)	2.98×10^{-6}	29.5	2.5-7.7	Ni^{2+} ions
5	4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one (30)	5.0×10^{-7}	19.7	2.7-6.6	Cr(III) ions
6	(2E, 3E)-2H-1,4-benzothiazine-2,3(4H)-dione dioxime (31)	1.6×10^{-6}	29.3	2-6.5	Ni^{2+} ions
7	1,4,8,11-tetraazacyclotetradecane (32)	5×10^{-7}	60	1.3-3.5	Fe(III) ions
8	1,3,5-trithiacyclohexane (33)	2×10^{-8}	19.8	5-8	La^{3+} ion
9	Bis-2-thiophenal propanediamine (34)	3×10^{-8}	29	3-7	Cu^{2+} ions
10	Hexathia-18-crown-6-tetraone (35)	1.3×10^{-6}	29	0.5-2.0	Hg^{2+} ions

Table4: Ionophore based CWEs for some rare earth metal ions

Sr. No.	**Name of Ionophore**	**Detection limit (M)**	**Slope mV/decade**	**pH range**	**Selectivity**
1	2,12-(2-methoxyaniline)2-4,14-Me2-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N6 (36)	5.8×10^{-9}	19.6	2.5-8.5	Yb^{3+}
2	3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetramethylacrylate-1,4,7,10,13,16-hexaazacyclooctadeca-3,13-diene) (37)	3.4×10^{-8}	19.8	2-8.5	Tb^{3+} ions
3	N′-[(2-Hydroxyphenyl)methylidene]-2-furohydrazide (38)	7.6×10^{-6}	19.4	3.5-10	Ce^{3+} ions
4	N-(thien-2-ylmethylene)pyridine-2,6-diamine (39)	8.0×10^{-7}	20.5	4.5-8	Lu^{3+} ions
5	N′-(2-Hydroxy-1,2-diphenylethylidene) benzohydrazide (HDEBH) (40)	7.0×10^{-8}	21	3.2-8.9	Er^{3+} ions
6	isopropyl 2-[(isopropoxycarbothioyl) disulfanyl]ethanethioate (41)	5×10^{-7}	21	4-7	Sm^{3+} ion
7	4,5,6,7-tetrathiocino[1,2:3,4]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione (Et_4todit) (42)	1.6×10^{-8}	6.5	4-6.5	Sm^{3+} ions
8	1,4-bis(3-thiapentylxanthato)butane (43)	5×10^{-7}	20	4.5-6.7	Sm^{3+} ions

Table5: Ionophore based CWEs for some anions

Sr. No.	Name of Ionophore	Detection limit (M)	Slope mV/decade	pH range	Selectivity
1	Bis(dibenzoylmethanato)Co(II) complex (44)	5.6×10^{-7}	-60.3	2-9	Per chlorate ions
2	Bis(dibenzoylmethanato)nickel (II) (45)	6.6×10^{-7}	-60	1.2-12.5	Perchlorate ions
3	Ether-cetyltrimethyl ammonium-thiocyanate (46)	0.03 µg ml−1	-57.6	3.8-9.2	SCN^{-}
4	1,3,5,8,10,13-hexaazacyclotetradecane (47)	6×10^{-7}	-59.5	3-11	Per chlorate ions
5	1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane–Ni(II) (48)	3×10^{-6}	-58.4		SCN^{-} ion
6	Unsymmetrical benzoN_4 nickel(II) macrocyclic (49)	1.4×10^{-7}	-59	3.5-10.5	SCN^{-}
7	Schiff base complex of Zn(II) (50)	8.5×10^{-8}	-29.3	3-7	SO_4^{2-} ion
8	Dinonylnaphthalene sulfonate (51)	1×10^{-6}	-59	3-8	DoTA (dodecyttrimethylammonium ion)
9	Tetrachloroferrate(III) salt of the quaternary ammonium compound, aliquat 3368 (52)	1×10^{-5}	-55	2-7.5	Tetrachloroferrate (III)

A comprehensive survey of the literature on coated-wire ion selective electrode shows that thiuram sulphides have not been as an ionophore in making silver selective electrode.This work describing the use of tetramethyl thiuram monosulphide and tetraethyl thiuram disulphide as an excellent-neutral ionophore for the prepration of a highly selective CWE for the potentiometric determination of Ag^{+} ion over a wide concentration range.

Chapter -3

Results & Discussion

3.1 Reagents and Apparatus

Reagents like ortho-nitrophenyl octyl ether (o-NPOE), tetraethyl thiuram disulphide, tetramethyl thiuram monosulphide were procured from Sigma-Aldrich. All other chemicals were of analytical reagent grade. Double distilled deionized water was used throughout the experiments. pH adjustments were made with dilute nitric acid or sodium hydroxide solutions as required. All potentials were measured with digital potentiometer and pH measurements were carried out on pH meter at room temperature (25 ± 0.1^0C) in stirred solutions. The salt bridge used here was Agar-Agar and KNO_3.

3.2 Fabrication of Coated Wire Ion Selective Electrode

Procedure for the membrane preparation (53) is as follows: Varying amount of Poly(vinyl chloride) (PVC) (33%), ortho-nitrophenyloctylether, o-NPOE ,ionophore were dissolved in 5-6 mL of THF. The solution was reduced to 2-3 mL by evaporation. To prepare electrode platinum wire was dipped in a highly viscous solution for several times. A membrane was formed on the platinum surface and it was allowed to evaporate in air for 5-6 hours. The electrode was conditioned by soaking in 0.1 M aqueous solution of $AgNO_3$ for 24 hours.

All emf measurements were carried out with the following electrochemical cell assembly:

$$\textbf{Hg-Hg}_2\textbf{Cl}_2\textbf{(s), KCl (sat)} \,||\, \textbf{Ag}^+ \textbf{ test solution} \,|\, \textbf{ionophore membrane} \,|\, \textbf{Pt wire}$$

3.3 Optimization of the Membrane Composition

Nature and amount of the membrane ingredients affect the sensitivity and selectivity of the electrode (54, 55). Performance characteristics of several membranes having different compositions for the fabrication of CWEs are shown in (**Table3)**. Increasing the ligand concentration improves the performance of the electrode in slope and detection limit and attained the best response in coated-wire ion selective electrode at 6% of TETDS and 6% of TMTMS. Membrane (E-3, E-7 in **Table3**) giving Nernstian slope was selected for further studies. In conventional system best response attained at 4% of TETDS, 4% of TMTMS. The results are shown in (M-2, M-6 in **Table4**). o-NPOE is the best plasticizer. Its high dielectric constant helps the ionophore in free movement and fast exchange in complexation and decomplexation between ionophore and silver ions.

3.4 Calibration Curve

The electrode shows a linear response towards Ag^+ ions over a wide concentration range of 1×10^{-5} M to 1×10^{-1} M . The calibration curve has a slope of 59 mV/decade with a detection limit of $1x10^{-5}$M obtained from the intersection of two straight line portions of the curve (**Figure2**) with TMTMS (E-7). The electrode shows a linear response towards Ag^+ ions over a wide concentration range of 1×10^{-6} M to 1×10^{-1} M . The calibration curve has a slope of 60 mV/decade with a detection limit of $1x10^{-6}$M obtained from the intersection of two straight line portions of the curve (**Figure3**) with TETDS (E-3). In conventional system, the electrode shows a linear response towards Ag^+ ions over a wide concentration range of 1×10^{-3} M to 1×10^{-1} M . The calibration curve has a slope of 48 mV/decade with a detection limit of $2.5x10^{-4}$M obtained from the intersection of two straight line portions of the curve with TETDS (M-2). The electrode shows a linear response towards Ag^+ ions over a wide concentration range of 1×10^{-5} M to 1×10^{-1} M. The calibration curve has a slope of 40 mV/decade with a detection limit of $1x10^{-5}$ M obtained from the intersection of two straight line portions of the curve with TMTMS (M-6). The reason for such behaviour is due to internal electrolyte contains salt of the primary ion, which however, induces a flux of these ions into the sample, thereby biasing the lower detection limit and selectivity co-efficient of the electrode (56).

3.5 Effect of pH

The potentiometric response of the proposed sensor was found to be sensitive to pH changes. Thus, the pH dependence of the electrodes was tested by measuring the potential response of solution containing 1.0 x 10^{-3} and 1.0 x 10^{-4} M of the Ag^+ ion in the pH range 2.0–10.The pH was adjusted by using 0.1 M solution of either HNO_3 or NaOH. The potential response of the electrode are shown in (**Figure4 and Figure5)**. It can be seen that potential response for electrode E-3 remains constant over the pH range 3.5–7.5 and for electrode E-7 remains constant over the pH range 5.0–8.5. Below and above this range the variation is due to interference from excess H^+ ions and hydrolysis of Ag^+ and formation of silver hydroxide.

3.6 Potentiometric Selectivity Coefficients

Selectivity of any chemical sensor is clearly one of its most important characteristics as this property often determines whether the sensor can be used reliably for the target sample or not. It was evaluated by fixed interference method (FIM) (57) as well as matched potential method (MPM). Interfering ion concentration was fixed at $1x10^{-2}$ M during $K_{i,j}$ determination by FIM. In case of matched potential method MPM. (58), a specified amount of primary ions is added to a reference solution and the membrane potential is measured. In a separate experiment, interfering ions are successively added to an identical reference solution until the membrane potential matches the one obtained before with the primary ion. The matched potential method selectivity coefficient is then defined by the ratio of the primary ion and interfering ion activities. From the data (**Table5**) it is obvious that there is no serious interference from the common ions., like Hg^{2+} and Pb^{2+}, alkali metal ions have more tendency to interfere. It may be because the metal ion charge is playing an important role in the selectivity determination process by FIM.

3.7 Effect of Mixed Solvent Medium

The real samples may contain mixed content, so the performance of the sensor was also investigated in partially non-aqueous media using 10%, 20%, 30% (v/v) using mixed content in methanol–water, acetone–water and DMSO–water mixtures . The membrane showed satisfactory response to Ag^+ ions in mixed solvent containing upto 30% (V/V) non-aqueous content. Results are summarized in (**Table6).** The best results are observed at 30% non-aqueous medium. The drift in potentials in the organic phase may be probably due to swelling in membrane which was too high that membrane became mechanically weak and leaching of ionophore from membrane to non-aqueous solution took place.

3.8 Direct and Reverse Titration of Ag^+ Ions

Known concentration of Ag^+ ions solution was titrated against standard solution of iodide ions. **Figure6** and **Figure7** show the observed potential break at 1:1 complex formation between metal ions and I^- ions. Potentiometric titrations are the most accurate because the emf follows the actual change in activity and therefore, the end point will often coincide directly with the equivalence point. A large potential break will occur at the equivalence point. Since we are interested only in the potential change, the absolute potential of the indicator electrode is not necessarily required. 50mL of solution containing $1x10^{-3}$ M Ag^+ ions was titrated against standard solution of KI (**Figure8 and Figure9**). In each titration only one break in EMF corresponding to AgI complex formation was observed. The titration shows an equivalence point corresponding to the formation of 1:1 complexes with I^- ions. The same observations were made during reverse titration also.

3.9 Simultaneous Determination of Halides from a Mixture

To establish the applicability of the proposed chemical sensor for Ag^+ ions, potentiometric titration of a mixture of halide ions containing equal concentrations of F^-, Cl^-, Br^- and I^- ions was carried out against $AgNO_3$. The proposed chemical sensor based on the ionophore was used as an indicator electrode. Titration curve shows four inflexion points corresponding to the precipitation of I^-, Br^-, Cl^- and F^- in the given sequence is shown in (**Figure10** and **Figure11**). A little deviation near the end of the titration for F^- ion may be due to relatively high solubility product value of AgF as compared to AgCl

($1x10^{-10}$) AgBr ($4x10^{-13}$) and AgI ($1x10^{-16}$). This application establishes that the electrode is a versatile chemical sensor for the determination of Ag^+ ions as well as the anions forming stable complexes or precipitates with Ag^+ ions.

Table6: Optimization of membrane ingredients for Ag^+-CWISE based on TETDS and TMTMS as ionophore

E. No.	Components of the membrane (% w/w)			Slope, (mV/decade)	Detection Limit, (M)	Working Concentration Range, from $1x10^{-1}$ (M)
	Ionophore (mg)	**PVC**	**Plasticizer (NPOE)**			
E-1	2	33	65	82	2.5×10^{-5}	1.0×10^{-4}
E-2	4	33	63	66	7.9×10^{-6}	1.0×10^{-5}
E-3	**6**	**33**	**61**	**60**	**1.0×10^{-6}**	**1.0×10^{-6}**
E-4	8	33	59	54	1.0×10^{-5}	1.0×10^{-5}
E-5	2	33	65	90	1.0×10^{-6}	1.0×10^{-5}
E-6	4	33	63	72	1.0×10^{-6}	1.0×10^{-5}
E-7	**6**	**33**	**61**	**59**	**1.0×10^{-5}**	**1.0×10^{-5}**
E-8	8	33	59	60	1.0×10^{-4}	1.0×10^{-4}

Table7: Optimization of membrane ingredients for Ag^+-CWISE based on TETDS and TMTMS as ionophore in conventional system

E. No.	Components of the membrane (% w/w)			Slope, (mV/decade)	Detection Limit, (M)	Working Concentration Range, from $1x10^{-1}$(M)
	Ionophore (mg)	**PVC**	**Plasticizer**			
M-1	2	33	65 (NPOE)	35	1.0×10^{-5}	1.0×10^{-3}
M-2	**4**	**33**	**63 (NPOE)**	**48**	**2.5 x 10^{-5}**	**1.0×10^{-3}**
M-3	6	33	61 (NPOE)	45	3.1×10^{-4}	1.0×10^{-3}
M-4	8	33	59 (NPOE)	42	1.0×10^{-4}	1.0×10^{-3}
M-5	2	33	65 (NPOE)	45	1.0×10^{-5}	1.0×10^{-5}
M-6	**4**	**33**	**63 (NPOE)**	**40**	**1.0×10^{-5}**	**1.0×10^{-5}**
M-7	6	33	61 (NPOE)	45	1.0×10^{-3}	1.0×10^{-3}
M-8	8	33	59 (NPOE)	48	1.0×10^{-4}	1.0×10^{-3}

Table8: Potentiometric selectivity coefficients for Ag^+-CWISE based on TMTMS and TETDS as ionophore

Interfering Ions (B)	$K_{Ag,B}^{Pot}$		$K_{Ag,B}^{Pot}$	
	TMTMS		**TETDS**	
	FIM	**MPM**	**FIM**	**MPM**
Na^+	.2	.1	.2	.1
Mg^{2+}	.06	.066	.063	.064
Ca^{2+}	6.3×10^{-3}	.0625	.060	.0625
Pb^{2+}	6.3×10^{-3}	6.2×10^{-2}	6.3×10^{-3}	6.2×10^{-2}
Cu^{2+}	6.3×10^{-3}	6.06×10^{-2}	6.3×10^{-3}	5.8×10^{-2}
Co^{2+}	.2	.066	.2	.066
Ni^{2+}	6.3×10^{-3}	5.7×10^{-2}	6.01×10^{-3}	5.7×10^{-2}
Zn^{2+}	.0632	.066	.0632	.066
Cd^{2+}	6.3×10^{-3}	6.3×10^{-2}	6.3×10^{-4}	6.4×10^{-2}
Hg^{2+}	2×10^{-3}	1.9×10^{-2}	2×10^{-3}	1.5×10^{-2}
Fe^{3+}	.02	.062	.02	.063

(**FIM**: Primary ion concentration varied from $1x10^{-1}$ M to $1x10^{-6}$ M, Interfering ion concentration $1x10^{-2}$ M.

MPM: Primary ion concentration $1x10^{-2}$ M –$1x10^{-4}$ M, reference solution $1x10^{-4}$ M and interfering ion concentration added $1x10^{-2}$ M)

Table9: Effect of Ag$^+$-CWISE based on TMTMS and TETDS as ionophore in mixed solvent media

Non-aqueous medium :water	Percentage, (V/V)	Slope, (mV/dec) (TETDS)	Detection limit, (M) (TETDS)	Slope, (mV/dec) (TMTMS)	Detection limit, (M) (TMTMS)
Water	--	59.0	$1.0x10^{-5}$	60.0	$1.0x10^{-5}$
Methanol:water	10:90	52.0	$1.9x10^{-5}$	64.0	$2.5x10^{-5}$
	20:80	54.0	$3.1x10^{-5}$	60.0	$3.1x10^{-5}$
	30:70	56.0	$3.9x10^{-5}$	62.0	$5.0x10^{-5}$
Acetone:water	10:90	52.0	$3.1x10^{-5}$	60.0	$3.9x10^{-5}$
	20:80	56.0	$5.0x10^{-5}$	54.0	$5.0x10^{-5}$
	30:70	57.0	$6.3x10^{-5}$	58.0	$6.3x10^{-5}$
DMSO:water	10:90	58.0	$1.0x10^{-5}$	58.0	$3.9x10^{-5}$
	20:80	60.0	$3.1x10^{-5}$	60.0	$6.3x10^{-5}$
	30:70	62.0	$5.1x10^{-5}$	56.0	$7.9x10^{-5}$

Table10: Comparing some of the Ag^+-CWISE characteristics with some previously reported Ag^+-ISEs

Name of the Ionophore	Slope (mV/ decade)	Linear Range, (M)	Interferent $K^{Pot}_{Ag,\ B}$	Response time (s)
1,4,8,11-tetraazacyclotetradecane (59)	59	1×10^{-4} to 1×10^{-7}	Na^+ (10^{-3}), Mg^{2+} (2.4×10^{-4}), Ca^{2+} (2.2×10^{-4}), Pb^{2+} (2.1×10^{-3}), Cu^{2+} (3.2×10^{-3}), Co^{2+} (7.9×10^{-3}), $Ni^{2+(}10^{-2}$), Zn^2 (7.9×10^{-3}), Cd^{2+} (10^{-3}), Hg^{2+} (6.3×10^{-3})	20
Octahydroxycalix[4]arene (10)	58	3.3×10^{-6} to 3.3×10^{-2}	Mg^{2+} (3.7×10^{-4}), Ca^{2+} (9.0×10^{-4}), Pb^{2+} (8.3×10^{-3}), Cu^{2+} (4.3×10^{-3}), Co^{2+} (8.0×10^{-3}), Ni^{2+} (7×10^{-5}), Zn^{2+}(10^{-5}), Cd^{2+} (10^{-4}), Fe^{3+}(1.9×10^{-3})	Less than 20
[Bz_2Oxo_4(18)dieneS_4] (60)	58	1.26×10^{-6} to 1.00×10^{-1}	Na^+ (8.6×10^{-4}), Mg^{2+} (4.3×10^{-5}), Ca^{2+} (2.9×10^{-4}), Pb^{2+} (2.5×10^{-3}), Cu^{2+} (3.5×10^{-3}), Co^{2+} (1.2×10^{-3}), Ni^{2+}(3.7×10^{-3}), Zn^{2+}(7.8×10^{-3}), $Cd^{2+(}2.9\times10^{-3}$), Hg^{2+}(2.1×10^{-2})	10
[bis 5-(4-nitrophenyl azo)salisylaldimine] 1,8-diamino, 3,6-dioxo octan (7)	56	2.7×10^{-2} to 1.9×10^{-6}	Mg^{2+} (1.9×10^{-4}), Ca^{2+} (1.9×10^{-4}), Pb^{2+} (3.9×10^{-3}), Cu^{2+} (3.1×10^{-3}), Co^{2+} (1.5×10^{-3}), Ni^{2+}(10^{-3}), Zn^{2+}(6.3×10^{-5}), Cd^{2+}(5.0×10^{-4}), Hg^{2+}(5.0×10^{-3})	5

Table11: Specifications of the Ag^+-CWISE based on TMTMS and TETDS

Properties	**TETDS**	**TMTMS**
Electrode type	Coated wire Pt electrode	Coated wire Pt electrode
Optimized membrane (wt%) PVC: Plasticizer: Ionophore	33: 61: 6	33: 61: 6
pH range	3.5-7.5	5.0-8.5
Linear range (M)	1.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-5} - 1.0×10^{-1}
Detection limit (M)	1.0×10^{-6}	1.0×10^{-5}
Slope (mV/decade)	60	59
Standard deviation	±2 mV at 10^{-4} (M) ±1 mV at 10^{-3} (M)	±2 mV at 10^{-4} (M) ±1 mV at 10^{-3} (M)
Response time (s)	~ 20	~25
Selectivity coefficients $K_{Ag,\ B}^{Pot}$	Na^+ (.2), Mg^{2+} (.06), Ca^{2+} (6.3×10^{-3}), Pb^{2+} (6.3×10^{-3}), Cu^{2+} (6.3×10^{-3}), Co^{2+} (.2), Ni^{2+}(6.3×10^{-3}), Zn^{2+}(.0632), Cd^{2+}(6.3×10^{-3}) ,Hg^{2+}(2.0×10^{-3}), Fe^{3+}(.02)	Na^+ (.2), Mg^{2+} (.063), Ca^{2+} (.060), Pb^{2+} (6.3×10^{-3}), Cu^{2+} (6.3×10^{-3}), Co^{2+} (.2), Ni^{2+}(6.3×10^{-3}), Zn^{2+}(.0632), Cd^{2+}(6.3×10^{-4}) ,$Hg^{2+(}2.0\times10^{-3}$), Fe^{3+}(.02)

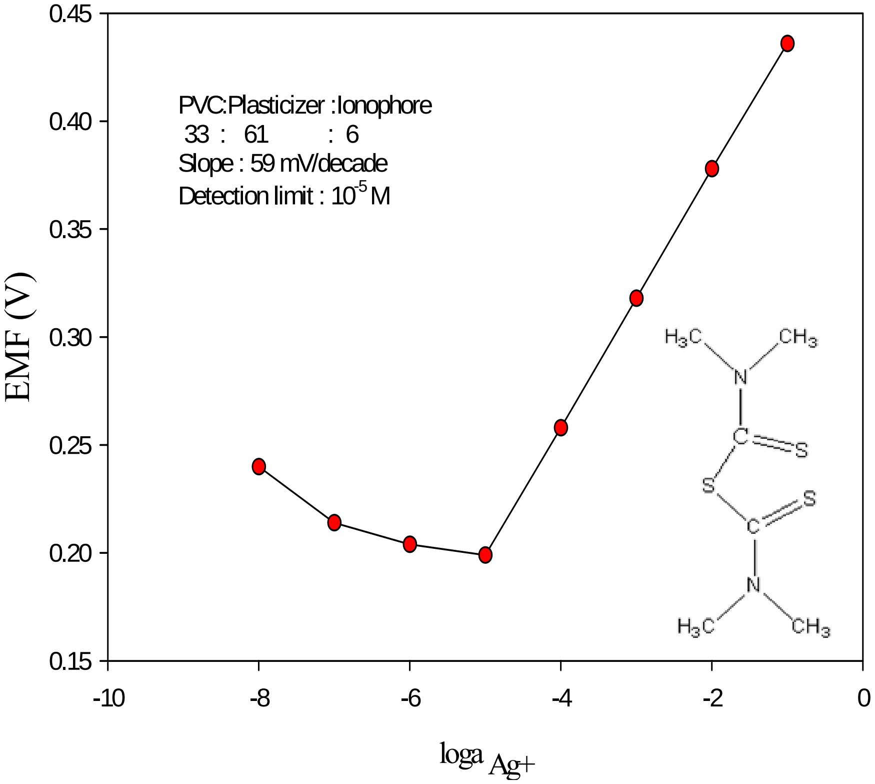


Figure2: Calibration curve for Ag^{+}-CWISE based on TMTMS (E-7)

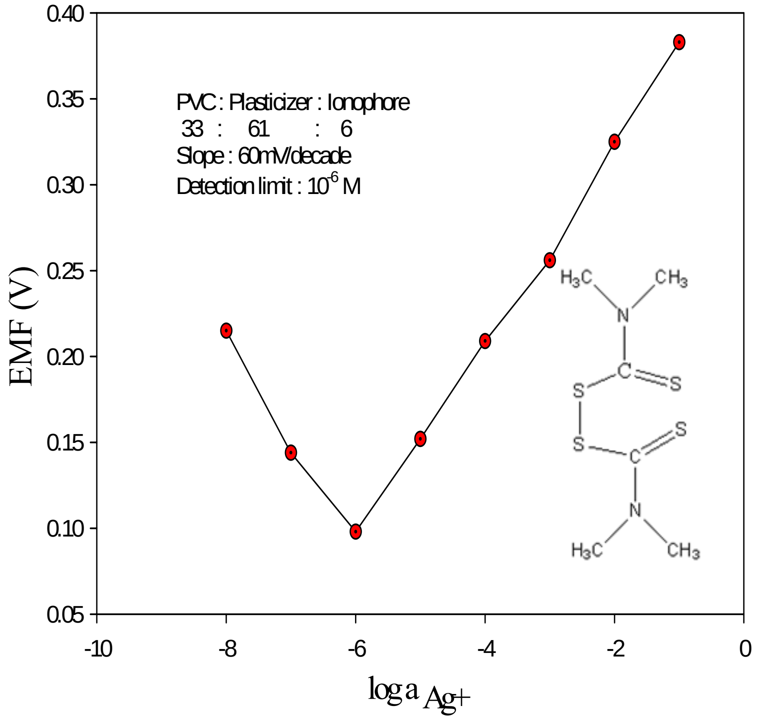


Figure3: Calibration curve for Ag^+-CWISE based on TETDS (E-3)

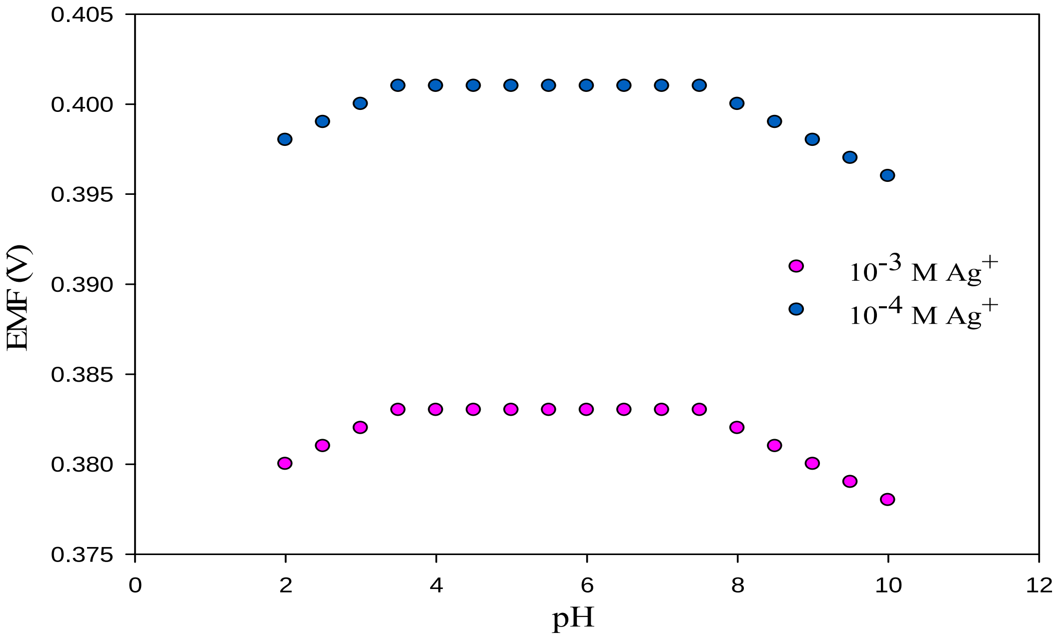


Figure4: Effect of pH on Ag^+-CWISE based on TETDS (E-3)

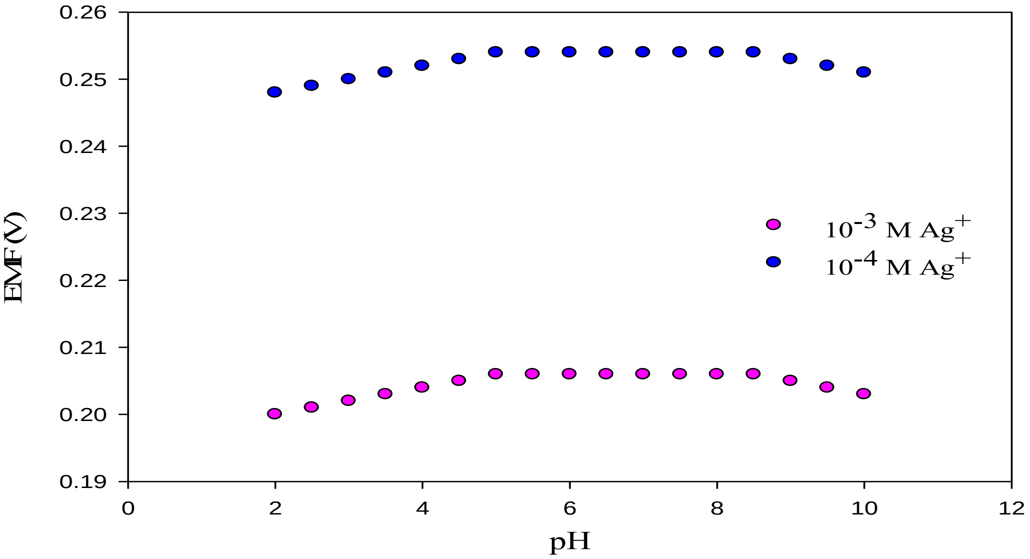


Figure5: Effect of pH on Ag^+-CWISE based TMTMS (E-7)

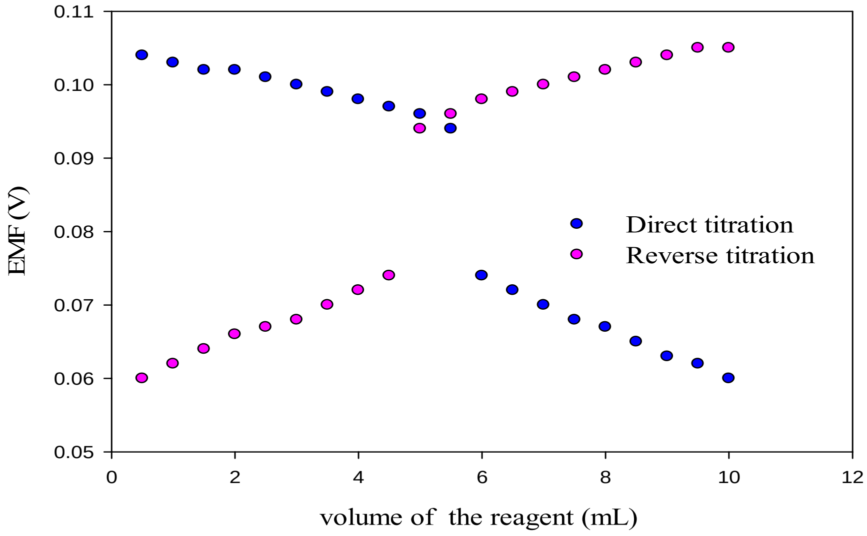


Figure6: Potentiometric titrations (Direct and Reverse) of Ag^+ ions versus I^- using (E-3) electrode

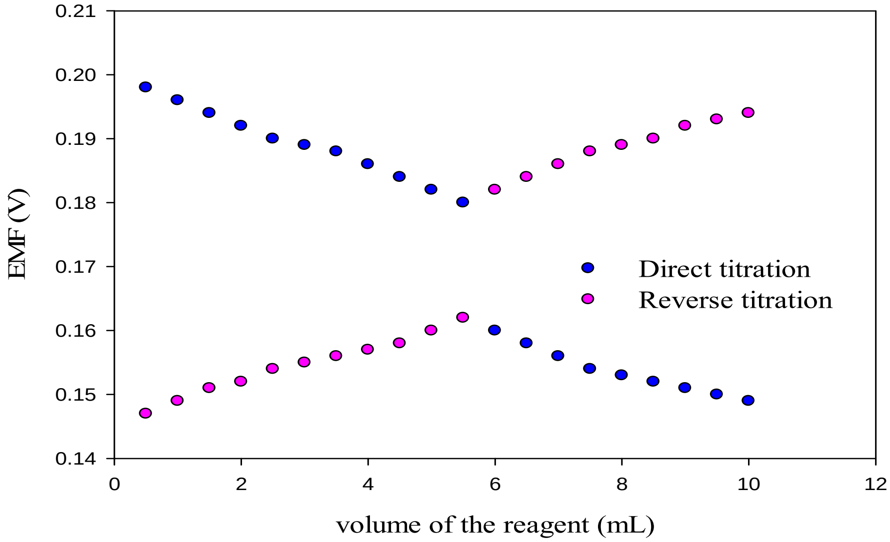


Figure7: Potentiometric titrations (Direct and Reverse) of Ag^+ ions versus I^- ions using (E-7) electrode

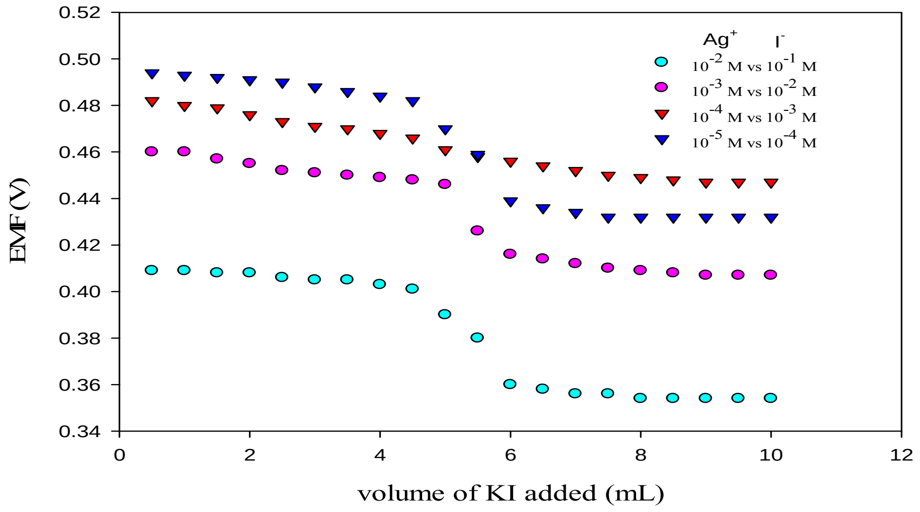


Figure8: Sensitivity of potentiometric titrations of (E-3) electrode to predict the detection limit

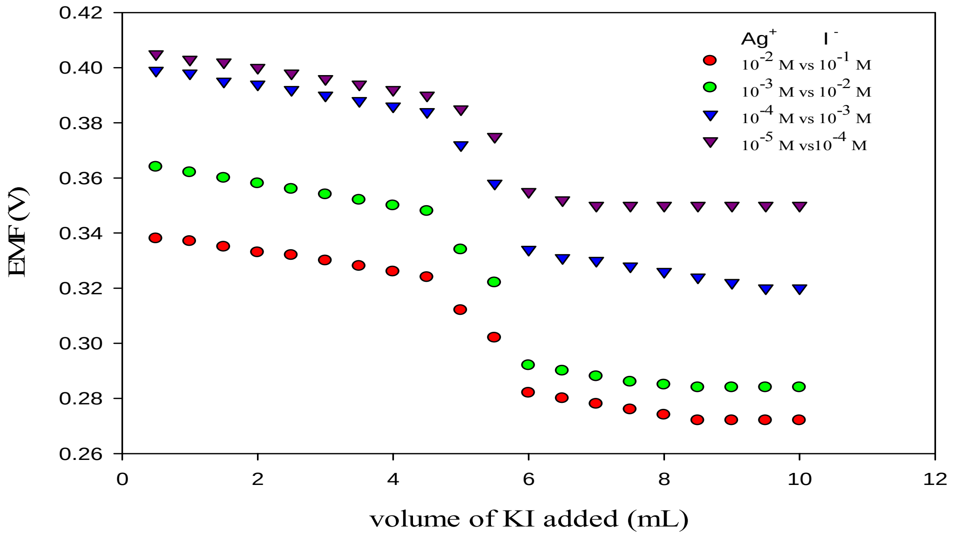


Figure9: Sensitivity of potentiometric titrations of (E-7) electrode to predict the detection limit

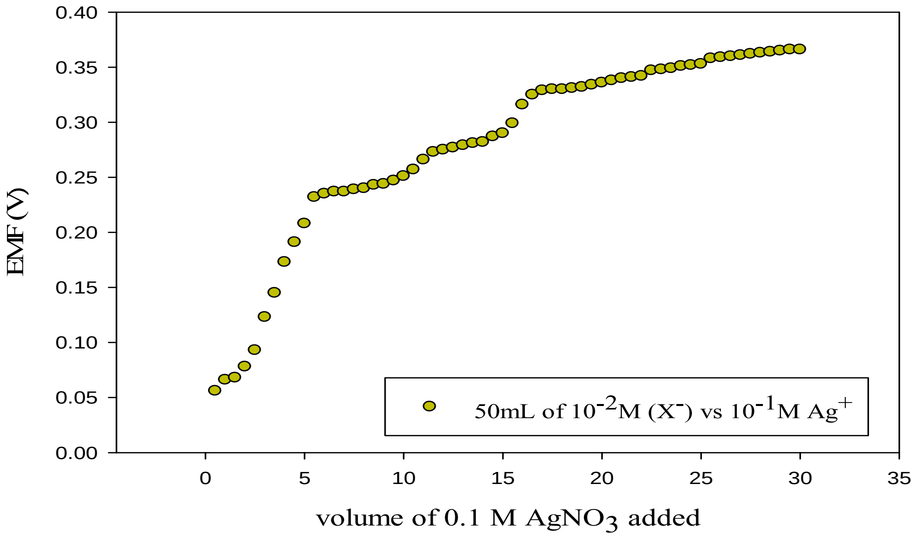


Figure10: Simultaneous determination of halide ions by potentiometric titration against Ag^+ ions using (E-3) electrode

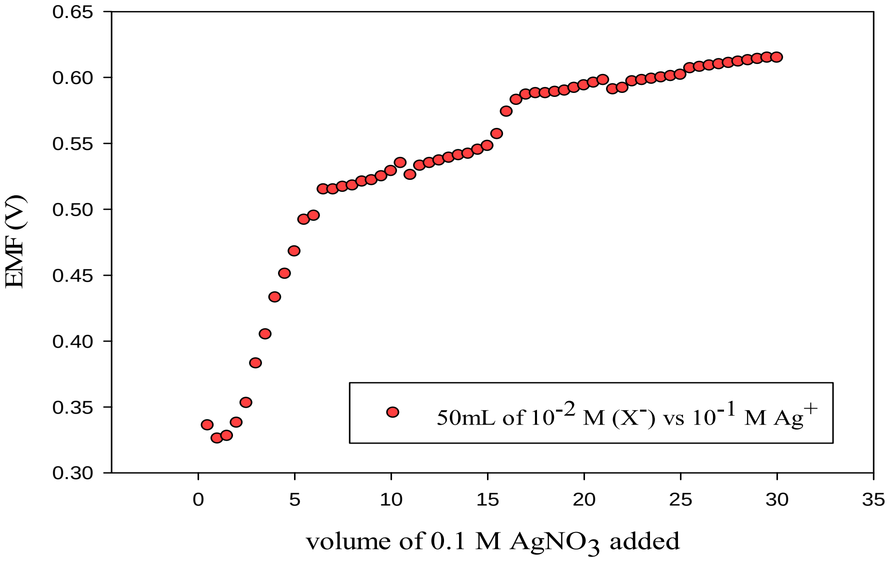


Figure11: Simultaneous determination of halide ions by potentiometric titration against Ag^+ ions using (E-7) electrode

Conclusions and future scope

On the basis of these results described in Table.6, the ligand tetraethyl thiuram disulphide(TETDS) and tetremethly thiuram monosulphide (TMTMS) can be regarded as a carrier for the construction of novel PVC based coated-wire ion selective electrode for silver. The electrode has been shown to have good operating characteristics (sensitivity, stability, response time, detection limit and a wide linear range). It is easy to prepare and use. This electrode can be used as a indicator electrode.

Polymetric membrance ion-selective electrodes have been identified for above to ions. In their most frequently used construction, the inner surface of the membrane is in contact with an internal solution which in turn surrounds the inner reference electrode. This arrangement guarantees high potential stability but has been shown to be, at least partly, the origin of zero-current trans-membrane ion fluxes. Conventionally, the internal electrolyte light contains a solution of primary ion, which however induces a flux of these ions into the sample, thereby biasing the lower detection limit and the measurement of selectivity co-efficient. By reducing compensating for these fluxes, the lower detection limit and selectivity behavior of a services of ISE have been improved by many orders of magnitude. Because the internal solution is at least in part, the source of such biasing effects, it is expected that ISE with a solid inner contact should have improved characteristics; They would also enable to true miniaturization without biasing selectivity and lower detection limit.

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